

## SPECIFICATION

### RELEASE AGENT FOR METALLIC MOLD

#### BACKGROUND OF THE INVENTION

##### 1. Field of the Invention.

The present invention relates to a release agent for metallic mold for forming ~~of~~ plastic molded products.

##### 2. Description of the Related Art

Plastics have excellent properties such as easy processability, high ~~productivity~~, light weight and relative low ~~procuring cost~~, so they are used for the parts and structural materials for ~~auto~~ mobile, ~~autobicycle~~, scooter, television, radio, audio equipment, washing machine, rice cooker, personal computer, portable telephone, game machinery, building ~~auto~~ materials, office supplies, stationery, toys, sports goods, sports equipment, ~~agricultural~~ agricultural tools and marine tools.

They are usually prepared by plastic processing methods such as injection molding, blow molding, compression molding, transfer molding, rotating molding, slush molding, inflation tubular film ~~process~~, and extrusion molding. ~~processes~~

As plastics ~~processing~~ are conducted at high ~~temperature~~ <sup>temperatures</sup> above 200°C, additives, monomers, decomposed materials in the plastics are changed to carbonized ~~auto~~-~~materials~~ materials such as tar, pitch and other ~~color~~ <sup>colored</sup> sticky substances, which are apt to adhere to the ~~surface~~ of the screw, ~~bar~~ <sup>surfaces</sup>

barrel, die and metallic mold of the plastic processing machine to cause transfer of the carbonized materials to the ~~met~~ ~~molded~~ ~~product~~ ~~products~~

Above mentioned transfer ~~make~~ makes the ~~sur~~ ~~surfaces~~ ~~make~~ ~~makes~~ face of molded ~~product~~ ~~products~~ dirty and ~~make~~ ~~makes~~ the dimensions of the molded product ~~un~~ ~~inaccurate~~ ~~inaccurate~~. As a result the molded product ~~do~~ ~~revised~~ ~~movement~~ ~~not~~ ~~perform~~ ~~expected~~ ~~moving~~ ~~or~~ ~~structural~~ ~~functions~~. Therefore clean-cleaning the screw, barrel, die and metallic mold of the plastic processing machine ~~machines~~ has been required.

In case of production ~~change~~ ~~from~~ ~~spe~~ ~~articles~~ ~~noncoloured~~ ~~articles~~ ~~different~~ ~~coloured~~ ~~molded~~ ~~articles~~ ~~coloured~~ ~~or~~ ~~other~~ ~~coloured~~ ~~molded~~ ~~articles~~, cleaning the screw, barrel and die has been ~~also~~ ~~required~~ to avoid ~~cross~~ ~~cont~~ ~~residual~~ ~~contamination~~ ~~amination~~ ~~caused~~ ~~by~~ ~~remained~~ ~~specifically~~ ~~compositions~~ ~~coloured~~ ~~resin~~ ~~compound~~ ~~associated~~ ~~with~~

However, there are some problems on the conventional ~~methods of~~ ~~cleaning~~ method of the screw, barrel, die and metallic mold.

There are ~~some~~ problems ~~occurring~~ ~~associated~~ with releasing the plastic molded ~~product~~ ~~products~~ ~~moles~~ from metallic mold.

The metallic mold for forming the plastic molded product has the complicated shapes with fine hollow and convex parts.

Therefore, the plastic molded product such as mechanical parts for electronic devices ~~automobiles~~ ~~have~~ ~~the~~ ~~complicated~~ ~~shapes~~. Consequently it is difficult to release the plastic mold product from metallic mold, because both surfaces ~~has~~ ~~shape~~ ~~hollow~~ ~~the~~ ~~complicated~~ ~~contrasting~~ ~~shape~~, which causes plastic mold product ~~ingrowing~~ to ~~products~~ ~~to~~ ~~ingress~~ into ~~caus~~ ~~↑~~ ~~the~~

partitions of

and become anchored thereto.

the metallic mold as if anchor bites the rock of bottom of the sea.

To avoid above mentioned difficulty of releasing both ~~surfaces~~, there ~~has~~ been efforts to treat ~~surfaces~~ there ~~has~~ been conducted to give activity to the interface between the metallic mold and the plastic molded product.

The method for giving activity to the interface involves using a lubricant has been conventionally used as the release agent for metallic mold molds.

The lubricant is usually applied by coating it onto the metallic mold ~~surfaces~~ <sup>that is</sup> surfaces.

However, when the metallic mold <sup>is</sup> coated with a conventional release agent was is

used for a long time, hard and uneven ~~he~~ heterogeneous layer was formed <sup>because of</sup> by the following reasons.

One reason is, accumulation of the resin and its additives such as antioxidant, metal deactivator, nucleating agent, anti-ultraviolet agent, antistatic agent, crosslinking agent, vulcanization agents and lubricants.

The other reason is, accumulation of the decomposition materials of resin and its additives.

The uneven shape on the surface of the metallic mold <sup>caused by the heterogeneous layer is</sup> apt to be transferred <sup>to</sup> the surface of the plastic molded product together with and the accumulated contaminants <sup>from the</sup> which will adhere surface of the metallic mold <sup>are</sup> adhered to the surface of the plastic molded product.

Above mentioned transferring of shape molded makes the dimensions of the plastic molded product inaccurate not to perform inaccurate

so that it will

~~required movement~~ ~~expected moving or structural function~~ ~~contaminants~~ ~~confounding~~ makes the surface of the plastic molded product dirty.

The hard and uneven heterogeneous layer on the surface of the metallic mold ~~fur~~ ~~surface~~ ~~adversely affects the~~ ~~face makes~~ ~~releasing property wrong~~ heterogeneous.

To remove the contaminants and heterogeneous layer ~~on~~ ~~from~~ the surface of the metallic mold, it is ~~common~~ ~~general way~~ to wash the soiled metallic mold after using ~~a predetermined~~ ~~time of~~ ~~examined time~~ facility ~~use~~.

At ~~the~~ plastic molded product ~~maker~~, washing is ~~carried~~ out after ~~the~~ troublesome task of taking the soiled metallic mold out from plastic processing machine, and ~~disassembling~~ ~~taking~~ the plastic mold ~~into~~ pieces, which requires ~~time~~ and ~~labor~~ ~~resulting in~~ to cause heavy loss of efficiency and cost.

Especially ~~at~~ ~~for~~ complicated or large sized metallic mold, removing, ~~dismantling~~ and washing work are tremendous to cause obstacles to improving the productivity and keeping cost down.

To decrease the number of times of ~~the~~ metallic mold washing, a release agent has been employed.

As the release agent, there ~~has~~ been known many <sup>known</sup> types of that such as dimethyl polysiloxane of <sup>the</sup> ~~non-crosslinking~~ <sup>crosslinking</sup> type, paraffin wax, higher fatty acid derivatives, metal soaps, talc, mica, and polytetrafluoroethylene of <sup>the</sup> ~~crosslinking~~ type, and the like.

However, conventional release agent ~~have~~ ~~has been pointed out~~ the following draw-

back drawbacks. of employing a non-crosslinking type  
In case employing noncrosslinking type  
of release agent, the release agent stay stays  
in a specific place of the metallic mold so as  
to affect adversely influence to the plastic  
molded product.

In the case of employing a crosslinking type of  
release agent, it exhibits the release agent will exhibit an  
excellent releasing property; however, said the release  
agent is apt to adhere to the surface of a  
plastic molded product to prevent the  
uniform painting or adhering treatment,  
resulting to decrease postprocessability.

In case of requiring a sufficient releasing  
effect to achieve a short shot cycle  
time, the amount of release agent must  
be increased, resulting to in accumulation  
and degradation of the release agent on the metallic mold. This causes adversely  
bad influence to the smooth and gross  
properties and the degradation of the mechanical  
strength such as tensile, elongate and  
anti-impact strength.

Further, it has become the problem that  
the release agent itself has decomposed  
by the high temperature heat transfer  
from the metallic mold.

For instance, dimethyl polysiloxane oil  
which is a representative release agent has temperature  
been gradually decomposed over the temperature  
of 150°C and has been rapidly decomposed  
over the temperature of 200°C to  
form viscous gel-like material which  
has become the problem to degrade the  
releasing property.

For improving the heat-resistant property

property of the said dimethyl polysiloxane, the use of there has been proposed the amino-group or mercaptogroup modified dimethyl polysiloxane. It has been proposed. discovered that

However, there has been detected the problem that said modified dimethyl polysiloxane has generated bad smell such as ammonia gas or mercaptan and has coloured the plastic molded products.

Also, dimethyl polysiloxane has been detected its problem that the release agent using dimethyl polysiloxane must has been prepared by dispersing it in the water to form the micelle by using a surface active agent, because dimethyl polysiloxane itself is not compatible with water.

The release agent using polytetrafluoroethylene has the drawback that it must be baked onto the surface of metallic mold. Therefore many troublesome repeating work of baking must be conducted notwithstanding its excellent releasing effect and secondary processing properties.

It is desirable that the release agent for metallic mold is prepared as an emulsion type from viewpoint of cost, applicability, toxicity, ignition, handling and applicability.

Emulsion type agent is prepared by method in which a surface active agent, water and non-water-soluble dimethyl polysiloxane oil or wax oil are agitated together to form micelles, which is able to be dispersed into water.

However, above mentioned surface active

the

~~agent~~ <sup>read</sup> reacts with the ingredients ~~bleed~~  
~~ed~~ from plastic molded ~~product~~ to form  
~~the~~ <sup>products</sup> ~~and~~ strong membrane (coated layer) on the  
surface of the metallic mold. <sup>IS</sup>

The membrane (coated layer) ~~has~~ hard  
and <sup>has an</sup> uneven heterogeneous shape ~~there~~  
~~fore the shape~~ <sup>which</sup> is transferred <sup>to</sup> ~~on~~ the <sup>surface</sup>  
~~ace of the~~ plastic molded ~~product~~ to  
~~cause~~ <sup>causing</sup> the problem of ~~producing~~ the out  
of standard plastic molded ~~product~~ <sup>products</sup>

On the other hand, when above mentioned  
release agent of <sup>the</sup> crosslinked type ~~by~~ <sup>that</sup> requires  
baking is used, the baked <sup>membrane</sup> (coa-  
~~coated~~ <sup>layer</sup>) ~~of exhibiting~~ <sup>that exhibits</sup> the releasing  
effect ~~has been~~ <sup>is</sup> gradually scraped <sup>off</sup> by the  
resin composition contacting ~~to~~ the  
metallic mold ~~at~~ <sup>during</sup> each injection shot. <sup>release</sup>

As the above mentioned baked type ~~re-~~  
lease agent is gradually scraped <sup>during</sup> ~~at~~ each  
shot of plastic resin composition into  
metallic mold, the release agent is  
removed from the surface of metallic  
mold ~~after~~ <sup>after</sup> ~~repeating shots of~~ <sup>are performed</sup> ~~repeating shots of~~ <sup>performed</sup>  
~~fresh~~ Then ~~from~~ <sup>from</sup> 10 to 20 shots ~~were over~~,  
~~new~~ release agent must be applied onto  
the surface of metallic mold, which is  
a very troublesome ~~work~~ task <sup>release</sup>

Further <sup>the</sup> above mentioned baked type ~~re-~~  
lease agent has the other problem owing  
~~to containing~~ <sup>of containing</sup> the reactive functional  
group such as amino, mercapto, isocyanate  
or vinyl group which is used for ~~condue~~ <sup>conducting</sup>  
~~ting~~ crosslinking and <sup>the</sup> baking reaction on  
the surface of metallic mold.

Owing to the reactive functional group,  
the surface energy of the ~~releasing~~  
<sup>release</sup>

agent layer on the metallic mold becomes very large to <sup>an</sup> increase <sup>in</sup> the frictional force between the surface of the plastic molded product and the surface of release ~~se~~ agent layer, which causes consumption of the release agent layer by scraping ~~by~~ <sup>during</sup> each injection shot, ~~resulting to~~ limiting ~~restrict~~ the life of <sup>the</sup> release agent layer ~~for~~ <sup>to</sup> ~~the~~ term of from 10 to 20 shots of injection mold ~~material~~.

~~The short life of the release agent requires less often time of the release agent by the baking treatment, which lead to accumulation of the unnecessary baked crosslinked release agent on the surface of the metallic mold, which adversely affects bad influence such as shape and contaminant transfer~~

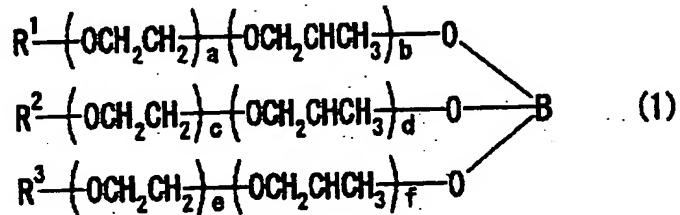
As mentioned above, conventional type ~~agents have drawbacks~~ release agent ~~has the drawbacks such as poor release effect, short durability term, difficult secondary processability and difficult treatment (baking) work on~~ <sup>application</sup> ~~onto~~ to the metallic mold.

#### SUMMARY OF THE INVENTION

As a result of diligent investigation ~~by~~ <sup>during the course of</sup> the present invention, under such situation, the present invention provides a release agent for metallic <sup>molded</sup> ~~for~~ <sup>for forming</sup> products <sup>which release agents</sup> ~~character~~ plastic molded product <sup>contain</sup> ~~characterized by~~ containing a borate ester of a polyoxyalkylene.

DETAILED DESCRIPTION OF THE  
INVENTION

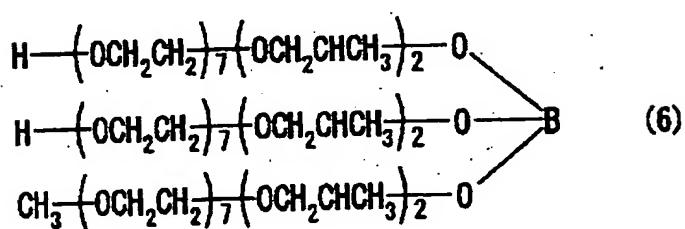
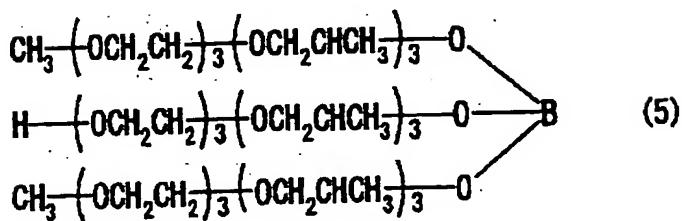
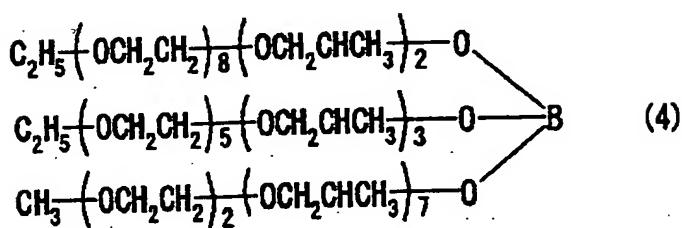
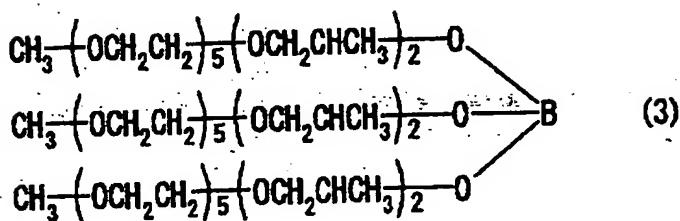
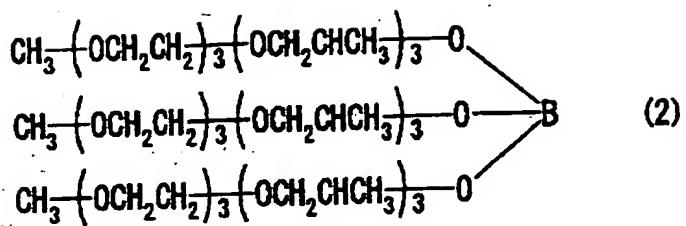
A borate ester of polyoxyalkylene used for the present invention is a chemical compound expressed by the following general formula (1).

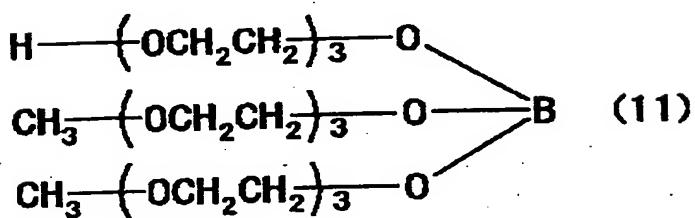
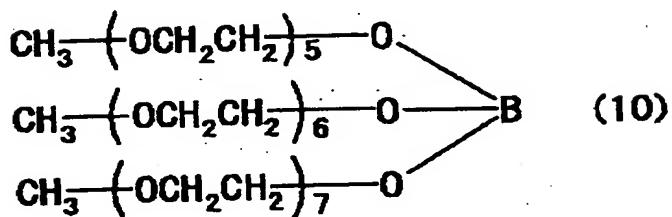
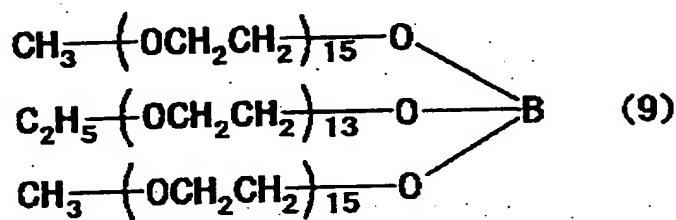
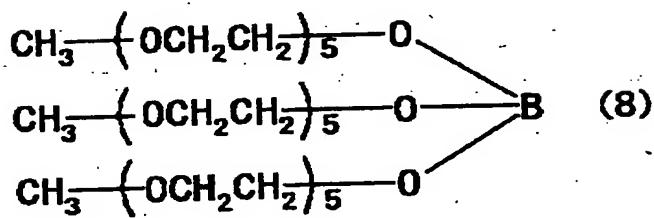
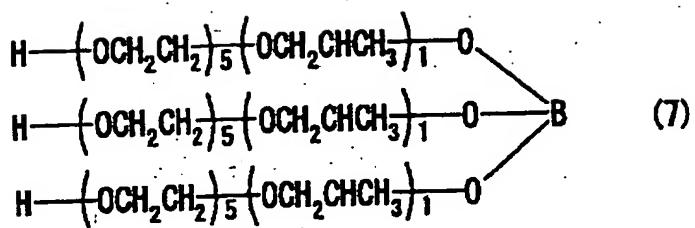


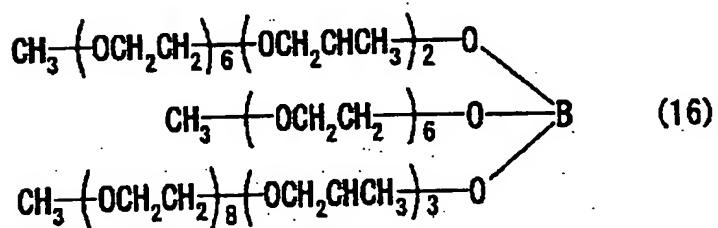
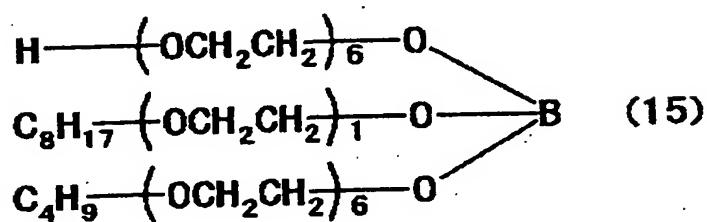
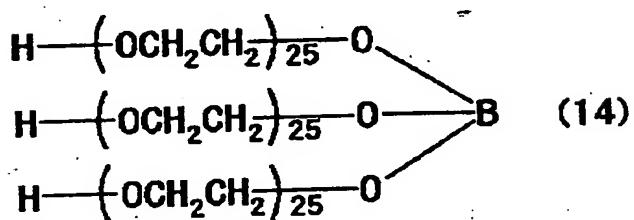
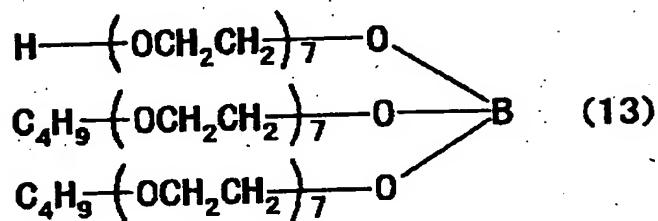
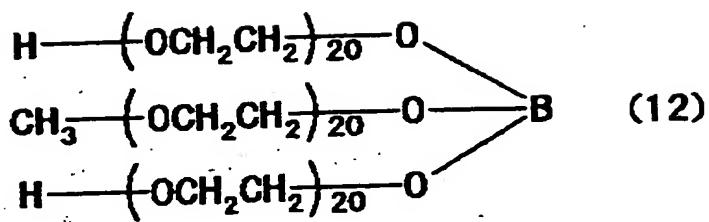
wherein  $R^1$ ,  $R^2$  and  $R^3$  are independently selected from the group consisting of ~~hydrogen~~ hydrogen and ~~a hydrocarbon group~~ ~~hydrogen and~~ ~~hydrocarbon group~~,  $a$ ,  $b$ ,  $c$ ,  $d$ ,  $e$  and  $f$  are positive integers independently selected from 0 to 30 whose sum is from 6 to 80.

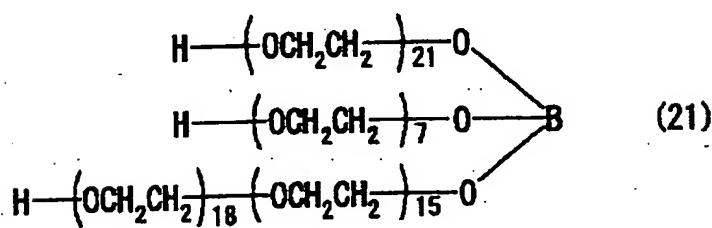
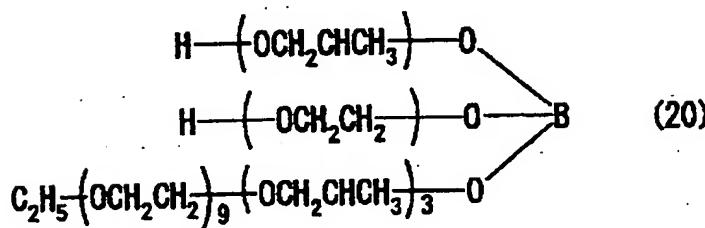
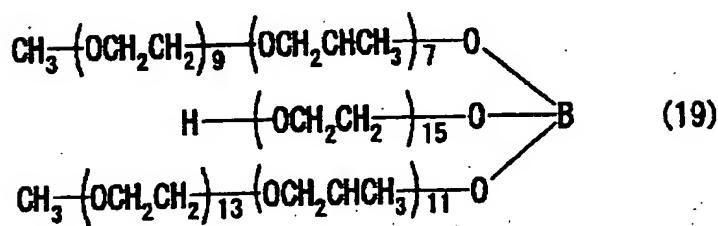
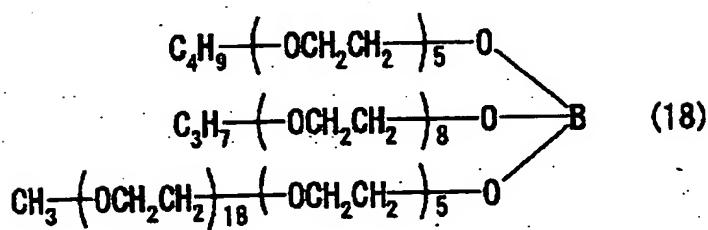
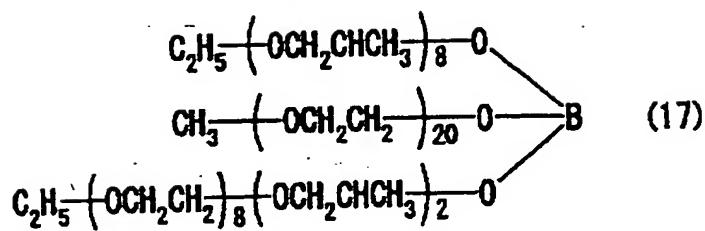
Example of the ~~hydrocarbon group~~ ~~hydrocarbon group~~ are alkyl groups such as methyl, ethyl, ~~propyl~~ <sup>propyl</sup>, ~~propyl~~, <sup>butyl</sup> <sup>propyl</sup>, isopropyl, ~~butyl~~, <sup>pentyl</sup> <sup>hexyl</sup>, ~~hexyl~~, <sup>octyl</sup> <sup>octyl</sup>, nonyl, decyl, dodecyl, hexadecyl, octadecyl and docosyl groups and phenyl, tolyl and cyclohexyl groups.

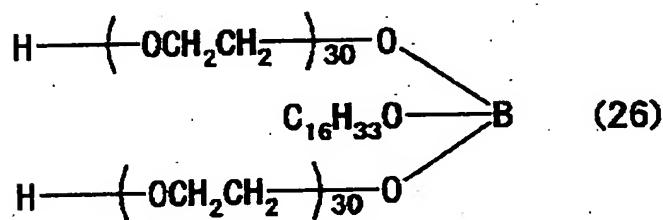
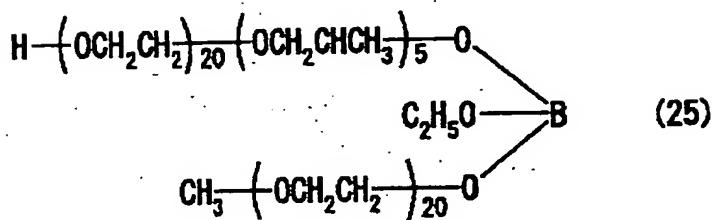
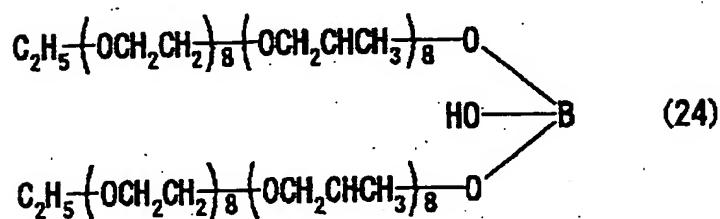
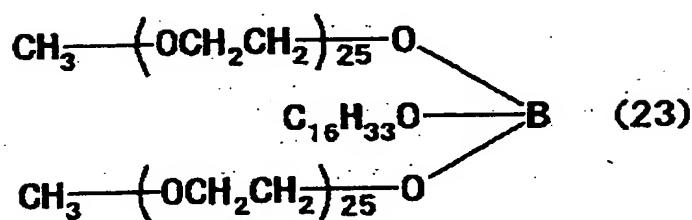
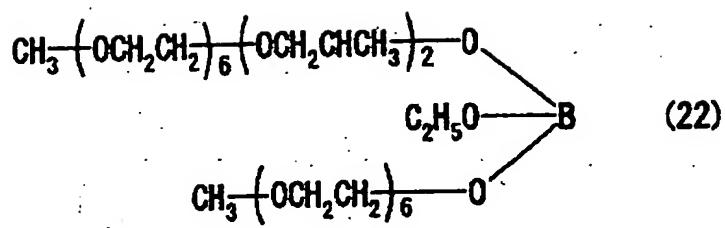
Illustrative of the borate ester of polyoxyalkylene are the chemical compounds expressed by the following chemical formula from (2) to (27).

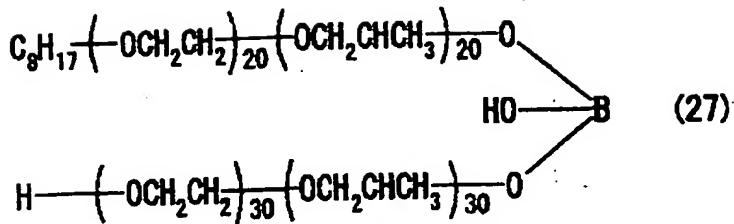








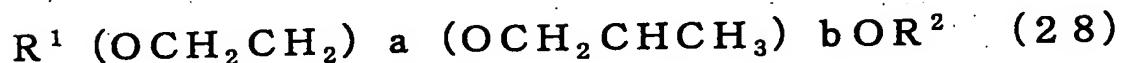




methods making the production method for borate esters of polyoxyalkylene used for the present invention are not limited to any specific method but following method is preferable. However, the preferred

The borate esters of polyoxyalkylene are produced by ~~esterification - dehydration~~ ~~esterification~~ ~~dehydration~~ ~~ester exchange~~ reaction by contacting a polyoxyalkylene expressed by the chemical formula (28) with ~~all~~ ~~alcohols~~ such as methyl alcohol or ethyl alcohol. It is preferable that the reaction is carried out by using 1 mol of boric acid or borate esters of lower alcohol with from 3 to 3.5 moles of polyoxyalkylene expressed by the chemical formula (28).

If the mole ratio is less than 3, it is not preferable because undesirable byproducts of borate esters having two or three boron atoms are generated. The other byproducts or unreacted polyoxyalkylene may remain in the borate esters unless they do not hinder the purging effect of the resin composition of the present invention.



wherein R<sup>1</sup> and R<sup>2</sup> are independently selected from a group consisting of hydrogen and hydrocarbon group, a and b are independently selected from 0 to 30.

Example Examples of the hydrocarbon group are alkyl groups such as methyl, ethyl, propyl, isopropyl, butyl, pentyl, hexyl, octyl, nonyl, decyl, dodecyl, hexadecyl, octa-octadecyl decyl and docosyl groups and phenyl, to tolyl and cyclohexyl groups.

Example Examples of the polyoxyalkylene expressed by the chemical formula (28) are as follows.

diethylene glycol monomethyl ether,  
diethylene glycol monoethyl ether,  
diethylene glycol monoisopropyl ether,  
diethylene glycol monobutyl ether,  
diethylene glycol monoethyl ether,  
diethylene glycol monodecyl ether,  
diethylene glycol monohexadecyl ether,  
diethylene glycol monooctadecyl ether,  
triethylene glycol monomethyl ether,  
triethylene glycol monoethyl ether,  
triethylene glycol monoisopropyl ether,  
triethylene glycol monobutyl ether,  
triethylene glycol monobutyl ether,  
triethylene glycol monoethyl ether,  
triethylene glycol monodecyl ether,  
triethylene glycol monohexadecyl ether,  
triethylene glycol mono-octadecyl ether,  
tetraethylene glycol monomethyl ether,  
tetraethylene glycol monoethyl ether,  
tetraethylene glycol monoisopropyl ether,  
tetraethylene glycol monobutyl ether,  
tetraethylene glycol monoethyl ether,  
mono-octyl

tetraethylene glycol monodecyl ether,  
tetraethylene glycol monohexadecyl ether,  
tetraethylene glycol monooctadecyl ether,

polyethylene glycol monomethyl ether,  
polyethylene glycol monoethyl ether,  
polyethylene glycol monoisopropyl ether,  
polyethylene glycol ~~monobutyl~~ ether,  
polyethylene glycol ~~monoocetyl~~ ether,  
polyethylene glycol ~~mono~~octyl ether,  
polyethylene glycol monodecyl ether,  
polyethylene glycol monohexadecyl ether,  
polyethylene glycol monoctadecyl ether,

dipropylene glycol monomethyl ether,  
dipropylene glycol monoethyl ether,  
dipropylene glycol monoisopropyl ether,  
dipropylene glycol ~~monobutyl~~ ether,  
dipropylene glycol ~~monoocetyl~~ ether,  
dipropylene glycol monodecyl ether,  
dipropylene glycol monohexadecyl ether,  
dipropylene glycol monoctadecyl ether,

tripropylene glycol monomethyl ether,  
tripropylene glycol monoethyl ether,  
tripropylene glycol monoisopropyl ether,  
tripropylene glycol ~~monobutyl~~ ether,  
tripropylene glycol ~~monoocetyl~~ ether,  
tripropylene glycol monodecyl ether,  
tripropylene glycol monohexadecyl ether,  
tripropylene glycol monoctadecyl ether,

tetrapropylene glycol monomethyl ether,  
tetrapropylene glycol monoethyl ether,  
tetrapropylene glycol monoisopropyl ether,  
tetrapropylene glycol ~~monobutyl~~ ether,  
tetrapropylene glycol ~~monoocetyl~~ ether,

tetrapropylene glycol monodecyl ether,  
tetrapropylene glycol monohexadecylether,  
tetrapropylene glycol monooctadecylether,  
  
polypropylene glycol monomethyl ether,  
polypropylene glycol monoethyl ether,  
polypropylene glycol monoisopropyl ether,  
polypropylene glycol monobutyl ether,  
polypropylene glycol monoethyl ether,  
polypropylene glycol monodecyl ether,  
polypropylene glycol monohexadecyl ether,  
polypropylene glycol mono-octadecyl ether,  
  
diethyleneglycol tripropyleneglycol  
monomethyl ether,  
tetraethyleneglycol dipropyleneglycol  
monomethyl ~~meth-ether~~,  
tetraethyleneglycol tripropyleneglycol  
monomethyl ether,  
tetraethyleneglycol tetrapropyleneglycol  
monomethyl ether,  
pentaethyleneglycol dipropyleneglycol  
monomethyl ether,  
pentaethyleneglycol tripropyleneglycol  
monomethyl ether,  
diethyleneglycol tetrapropyleneglycol  
monomethyl ether,  
  
hexaethyleneglycol dipropyleneglycol  
monomethyl ether,  
hexaethyleneglycol dipropyleneglycol  
monomethyl ~~meth-ether~~,  
hexaethyleneglycol tripropyleneglycol  
monomethyl ether,  
hexaethyleneglycol tetrapropyleneglycol  
monomethyl ether,

hexaethyleneglycol pentapropylene glycol  
monomethyl ether,

hexaethyleneglycol hexapropylene glycol  
monomethyl ether,

heptaethyleneglycol dipropylene glycol  
monomethyl ether,

heptaethyleneglycol dipropylene glycol  
monomethyl ~~meth~~ ether,

heptaethyleneglycol tripropylene glycol  
monomethyl ether,

heptaethyleneglycol tetrapropylene glycol  
monomethyl ether,

heptaethyleneglycol pentapropylene glycol  
monomethyl ether,

heptaethyleneglycol hexapropylene glycol  
monomethyl ether, *heptapropylene glycol*

heptaethyleneglycol ~~heptapropylene gly-~~  
~~col~~ monomethyl ether,

octaethyleneglycol dipropylene glycol  
monomethyl ether,

octaethyleneglycol tripropylene glycol  
monomethyl ~~meth~~ ether,

octaethyleneglycol tetrapropylene glycol  
monomethyl ether,

octaethyleneglycol pentapropylene glycol  
monomethyl ether,

octaethyleneglycol hexapropylene glycol  
monomethyl ether,

octaethyleneglycol heptapropylene glycol  
monomethyl ether,

polyethyleneglycol polypropylene glycol  
monomethyl ether,

triethylene glycol,

tetraethylene glycol,  
pentaethylene glycol,  
hexaethylene glycol,  
heptaethylene glycol,  
octaethylene glycol,  
decaethylene glycol,  
tridecaethylene glycol,  
hexadecaethylene glycol,  
eicosaeethylene glycol,  
pentacosaeethylene glycol,  
triacosaeethylene glycol,

tripropylene glycol,  
tetrapropylene glycol,  
pentapropylene glycol,  
hexapropylene glycol,  
heptapropylene glycol,  
octapropylene glycol,  
decapropylene glycol,  
tridecapropylene glycol,  
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pentacosapropylene glycol,  
triacosapropylene glycol,

triethylene glycol tripolypropylene glycol,  
tetraethylene glycol dipropylene glycol,  
tetraethylene glycol tripolypropylene glycol,  
tetraethylene glycol tetrapropylene glycol,  
pentaethylene glycol dipropylene glycol,  
pentaethylene glycol tripolypropylene glycol,  
hexaethylene glycol dipropylene glycol,  
hexaethylene glycol tripolypropylene glycol,  
hexaethylene glycol pentapropylene glycol,

hexaethylene glycol hexapropylene glycol,  
heptaethylene glycol dipropylene glycol,  
triacosaethylene glycol dipropylene  
glycol,

heptaethylene glycol tripropylene glycol,  
heptaethylene glycol tetrapropylene  
glycol,

heptaethylene glycol pentapropylene  
glycol,

heptaethylene glycol hexapropylene  
glycol,

heptaethylene glycol heptapropylene  
glycol,

octaethylene glycol dipropylene glycol,  
octaethylene glycol tripropylene glycol,  
octaethylene glycol tetrapropylene  
glycol,

octaethylene glycol pentapropylene  
glycol,

octaethylene glycol hexapropylene glycol,  
octaethylene glycol pentapropylene  
glycol,

octaethylene glycol octapropylene glycol,  
polyethylene glycol polypropylene glycol,

tripropylene glycol triethylene glycol  
monomethyl ether,

tetrapropylene glycol diethylene glycol  
monomethyl ether,

tetrapropylene glycol triethylene glycol  
monomethyl ether,

tetrapropylene glycol tetraethylene  
glycol monomethyl ether,

pentapropylene glycol diethylene glycol

monomethyl ether,  
pentapropylene glycol triethylene glycol  
monomethyl ether,  
pentapropylene glycol tetraethylene  
glycol monomethyl ether,

hexapropylene glycol diethylene glycol  
monomethyl ether,  
hexapropylene glycol triethylene glycol  
monomethyl ether,  
hexapropylene glycol tetraethylene  
glycol monomethyl ether,  
hexapropylene glycol pentaethylene  
glycol monomethyl ether,  
hexapropylene glycol hexaethylene glycol  
monomethyl ether,

heptapropylene glycol diethylene glycol  
monomethyl ether,  
heptapropylene glycol triethylene glycol  
monomethyl ether,  
heptapropylene glycol tetraethylene  
glycol monomethyl ether,  
heptapropylene glycol pentaethylene  
glycol monomethyl ether,  
heptapropylene glycol hexaethylene  
glycol monomethyl ether,  
heptapropylene glycol heptaethylene  
glycol monomethyl ether

octapropylene glycol diethylene glycol  
monomethyl ether,  
octapropylene glycol triethylene glycol  
monomethyl ether,  
octapropylene glycol tetraethylene  
glycol monomethyl ether,

octapropylene glycol pentaethylene glycol monomethyl ether,  
octapropylene glycol hexaethylene glycol monomethyl ether,  
octapropylene glycol heptaethylene glycol monomethyl ether  
octapropylene glycol octaethylene glycol monomethyl ether  
polypropylene glycol polyethylene glycol monomethyl ether

tripropylene glycol triethylene glycol monomethyl ether,  
tetrapropylene glycol triethylene glycol monomethyl ether,  
tripropylene glycol triethylene glycol monomethyl ether,  
octapropylene glycol diethylene glycol monomethyl ether,  
octaethylene glycol dipropylene glycol monomethyl ether,  
octaethylene glycol tripropylene glycol monomethyl ether,  
octaethylene glycol tetrapropylene glycol monomethyl ether,  
octaethylene glycol pentapropylene glycol monomethyl ether,  
octaethylene glycol hexapropylene glycol monomethyl ether,  
octaethylene glycol heptapropylene glycol monomethyl ether,  
octaethylene glycol octapropylene glycol monomethyl ether,  
polyethylene glycol polypropylene glycol monomethyl ether.

incorporated

A solvent or diluent may be incorporated into the raw materials such as boric acid, borate ester of lower alcohol and polyoxyalkylene, or into the borate esters of polyoxyalkylene.

If the solvent or diluent are employed, they must not disturb the esterification-dehydration or ester-exchange reaction and their boiling points should preferably be below the boiling point of the byproducts or polyoxyalkylenes.

Examples of the solvents or diluents are ethers such as diethyl ether, dioxane, tetrahydrofuran; aliphatic hydrocarbons such as hexane, acetic anhydride, heptane, octane, nonane, decane, undecane; aromatic hydrocarbons such as benzene, toluene, xylene; cycloalkanes such as cyclohexane, cyclohexene; non-proton polar compounds such as dimethyl formamide, di-dimethyl methyl sulfoxide, hexamethyl polyamide phosphate, acetonitrile, N-methyl pyrro-pyrrolidone; lidones, and their chlorine substituted compounds such as chloroform and carbon tetrachloride.

A catalyst for the esterification-dehydration or ester-exchange reaction may be used.

If the catalysts are necessary for promoting the reaction, following condensation catalysts are recommended.

Examples of the catalysts are metallic salts of organic acids such as ferrous octanoate, ferrous naphthenate, cobaltous naphthenate, manganese octanoate, stannum octanoate, stannum naphthenate, lead

octanoate, lead naphthenate, organotin  
~~compounds~~ such as ~~dibutyl~~ tin ~~dibutyl~~ diacetate,  
~~dibutyl~~ tin ~~dibutyl~~ dioctanoate, ~~dibutyl~~ tin ~~dibutyl~~  
dilaurate, ~~dibutyl~~ tin ~~dibutyl~~ dioleate, ~~dibutyl~~ tin ~~dibutyl~~  
tin dimethoxide, oxidized ~~dibutyl~~ tin;  
metal ~~alcohohates~~ such as tetrabutyl ~~tin~~ ~~titanoate~~  
~~chelates~~ such as di-isopropoxy bis-acetyl  
acetone titanum, 1, 3-propanedioxy ~~3-propanedioxy~~  
bis-ethylacetone titanum, 1, ~~3-propanedioxy~~  
~~nedioxy~~ bis-ethylacetatoacetate titanum;  
~~aluminum chelates~~ such as ~~aluminum acetyl~~  
~~aluminum~~ ~~tris-ethylacetatoacetate~~  
acetone, ~~aluminum~~ ~~tris-ethylacetatoacetate~~  
nate; amines such as hexyl amine, ~~dodecylamine~~  
~~ethylamine~~ phosphate, dimethyl ~~hydroxy~~ ~~hydroxylamine~~  
~~amine~~, diethyl hydroxylamine; tetra ~~ammonium~~ ammonium  
~~salt~~ such as benzyl hydroxylamine;  
inorganic ~~acid~~ such as ~~hydrochloric~~ acid,  
nitric acid, ~~sulfuric~~ acid, phosphoric ~~anhydride~~  
~~acid~~; organic ~~acid~~ such as acetic ~~anhydride~~  
~~ride~~, pure acetic acid (over 99.8%), ~~propionic~~  
~~acid~~, citric acid, benzoic acid,  
~~formic~~ acid, acetic acid, oxalic acid,  
p-toluenesulfonic acid; ~~chlorosilane~~ ~~chlorosilanes~~  
such as methyl trichlorosilane, dimethyl  
dichlorosilane; inorganic ~~base~~ such as  
aqueous ammonia; organic ~~base~~ such as  
ethylene diamine, triethanol amine; and  
amino alkylamine.

It is preferable that the ~~esterification~~ ~~dehydration~~ ~~reaction~~  
~~dehydration~~ or ester exchange ~~reaction~~  
is carried out under the condition  
of a reduced or atmospheric pressure, and at a temperature  
from 50 to 250°C ~~temperature~~, favourably  
from 100 to 180°C. and preferably

During the reaction, removal of ~~bypro-~~  
~~byproducts~~

alcohols  
ducts such as lower alcohol or water can  
~~precede~~ proceed the reaction easily because removal  
of byproducts ~~precede~~ <sup>prevents</sup> the reaction  
equilibrium to favorable ~~the formation~~ <sup>the formation</sup>  
borate ester <sup>esters</sup> of polyoxyalkylenes formation.

As to the removal method, azeotropic distillation using azeotropic agent and batch or continuous distillation using distillation tower are preferable.

For the purpose of improving the properties of the borate ester of polyoxyalkylenes, amino-group containing compounds and and/or solvent may be added to said the borate esters of polyoxyalkylenes.

Adding the amino-group containing compound to the borate ester of polyoxyalkylenes ~~causes~~ <sup>improves</sup> suppression of borate ester hydrolysis and also exhibits preventive effects <sup>caused by the</sup> under the condition of ~~existence~~ <sup>the</sup> ~~existence~~ of water or its vapor.

Examples of the amino-group containing compound include alkylamine, cyclo alkyl amine, alkanol amine, heterocyclic amine, diamine, lactam, cyclic imide and poly-polyamino amine, which may be used alone or combination selecting from these compound.

As the alkyl amine, there can be used methyl amine, dimethyl amine, trimethyl amine, ethyl amine, diethyl amine, triethyl amine, propyl amine,  $N,N$ -di[poly- $N,N$ -di[poly(4)-(4)-oxyethyl] hexadecyl] amine, dodecyl dimethyl amine, stearamide propyl dimethyl amine, polyoxyethylene (3-30) octa-octadecyl deoxy amine, polyoxyethylene (3-30) lauryl

amine, polyoxyethylene (3-30) oleyl amine, polyoxyethylene (3-30) dilauryl amine, polyoxyethylene (3-30) stearyl amine, polyoxyethylene (3-30) alkyl amine, ~~polyoxyethylene (3-30)~~ polyoxyethylene (3-30) dialkyl amine, and di (oleoyloxyethyl) hydroxy amine.

As the cycloalkyl amine, there can be used cyclohexyl amine, methyl cyclohexyl amine and ethyl cyclohexyl amine.

As the alkanol amine, there can be used ethanol amine, diethyl hydroxy methyl amine, diethanol amine, dimethyl ~~amine~~ <sup>aminoethanol</sup> ethanol, triethanol amine, propanolamine, dimethyl 2-hydroxypropyl amine, butanol amine, methyl di (2-hydroxyethyl) amine, tri (2-hydroxyethyl) amine, hydroxymethyl di (2-hydroxyethyl) amine, dibenzil 2-hydroxypropyl <sup>2-hydroxypropyl</sup> amine and cyclohexyl di (2-hydroxyethyl) amine.

As the cycloalkanol amine, there can be used cyclohexanol amine, ~~methylcyclo-~~ <sup>methylcyclohexanol</sup> hexanol amine and ethylcyclohexanol amine.

As the heterocyclic amine, there can be used ~~and~~ pyridine, lutidine, 3, 4-xylidine, piperidine, N-methyl piperidine and N-ethyl piperidine.

As the lactam, there can be used propio lactam, N-methylpropio lactam, N-ethyl <sup>butyro</sup> lactam, N-methyl varero lactam, N-methyl caprolactam and phenyl caprolactam.

As the cyclic imide, there can be used succinimide, N-methyl succinimide, ~~N- N-ethyl~~ ethyl succinimide, phenyl succinimide and 2-undecyl imidazoline.

As the diamine, there can be used ethylene diamine, triethylene diamine and tetraethylene diamine.

As the polyamine, there can be used diethylene triamine, triethylene tetra-~~amino~~ diamine and pentaethylene pentamine.

Among these ~~amino-group~~ containing compounds, tertiary ~~amino-group~~ containing compounds exhibit <sup>an</sup> excellent effect of preventing hydrolysis of borate ester of polyoxyalkylene and ~~promote~~ <sup>cleaning</sup> promoting the cleaning and purging the ~~coloured~~ colored contaminants.

Example  
Example of tertiary ~~amino-group~~ containing compounds having <sup>the</sup> above mentioned excellent properties are polyoxyethylene (3-30) octadecyl amine, ~~polyoxyethylene(3-30)~~ (3-30) lauryl amine, polyoxyethylene (3-30) oleyl amine, polyoxyethylene (3-30) ~~di-alkyl~~ <sup>polyoxyethylene(3-30)</sup> amine, polyoxyethylene (3-30) stearyl amine, polyoxyethylene (3-30) alkyl amine, polyoxyethylene (3-30) dialkyl amine.

The amount of ~~amino-group~~ containing compound to 100 parts by weight of the borate ester of polyoxyalkylene is from 0 to 100 parts by weight, ~~favourably and preferably~~ from 5 to 50 parts by weight and most ~~preferably~~ ~~favourably~~ from 10 to 30 parts by weight.

Use of the solvent contributes to a lower viscosity of the borate ester of polyoxyalkylene.

As the solvent, there can be used water, methyl alcohol, ethyl alcohol, isopropyl alcohol, butyl alcohol, ~~iso-~~ <sup>150</sup> ~~propyl~~ propyl ether, ether, ethylene glycol, polyethylene glycol, polyethylene di-~~dimethyl~~

methyl ester, diethylene glycol, tri- triethylene glycol, ethylene glycol, ethylene glycol di- dimethyl methyl ether, diethylene glycol di- dimethyl methyl ether, diethylene glycol diethyl ether, ethylene glycol dipropyl ether, triethylene glycol dimethyl ether, triethylene glycol monobutyl ether, diethylene glycol monobutyl ether, di- diethylene glycol diethyl ether, diethylene glycol propyl ether, diethylene glycol dibutyl ether, dimethyl ether, pro- propylene glycol, acetone, methylethyl keto- ketone, furfural, dioxane, methane sulfonate, diethyl ether, tetra hydrofuran, hexane, acetic anhydride, heptane, octane, nonane, decane, undecane, benzene, toluene, xylene, cyclohexane, cyclohexene, dimethyl formamide, dimethyl sulfoxide, hexa- heptamethyl methyl triamide phosphate, acetonitrile, N-methyl pyrrolidone, chloroform and carbon tetrachloride and <sup>these</sup> the solvents can be used alone or in combination.

The amount of solvent to 100 parts by weight of borate ester of polyoxalkylene and amino-group containing compound are respectively from 0 to 100 parts by weight, and preferably from 5 to 50 parts by weight and most preferably from 10 to 30 parts by weight.

Ingredients  
The other ingredient other than amino-group containing compound and/or solvent may be incorporated into the polyoxalkylene for the purpose of improving the properties of the release agent of the present invention.

As the other ingredient, there can be

Ingredients

used stabilizer, neutralizer, ~~antiox~~<sup>antioxidants</sup>, ~~stabiliz~~<sup>stabilizers</sup>, ultraviolet absorber, light stabilizer, antistatic agent, lubricant, ~~pro-processor~~<sup>processability</sup>, ~~cessability~~ improving agent, ~~filler~~<sup>fillers</sup>, dispersing agent, coupling agent, ~~anti-copper~~<sup>anti-copper</sup>, copper rusting agent, blowing agent, ~~ne-~~ nuclear clear forming agent, ~~anti-forming~~<sup>anti-forming</sup> agents, deformer, ~~colorant~~<sup>colorants</sup>, pigment, ~~dyeing~~<sup>dyeing</sup> agents, carbon black, water tree prevent ~~pre-~~<sup>preventing</sup> agent, voltage stabilizer, ~~anti-trac-~~<sup>anti-tracking</sup> king agent, organic peroxide, ~~crosslink-~~<sup>crosslink-</sup> ~~crosslinking~~<sup>crosslinking</sup> agent, disinfectant, ~~anti-septics~~<sup>anti-septics</sup>, ~~anti-mold~~<sup>anti-mold</sup> agent and ~~anti-rust~~<sup>anti-rust</sup> agent.

In the present invention, a release agent for metallic mold means ~~the~~<sup>a</sup> release agent which is coated on the surface of a metallic mold used for plastic or gum processing to prevent ~~the~~ adhesion ~~between~~<sup>between</sup> ~~the~~ metallic mold and plastic ~~product~~<sup>product</sup> molded ~~there~~<sup>there</sup> the release ~~product~~<sup>product</sup> resulting to make the plastic ~~product~~<sup>product</sup> easily separate from the metallic mold.

The ~~metallic~~<sup>metallic</sup> molds ~~to~~ for which the release agent of the present invention ~~is~~<sup>are</sup> applicable ~~agents~~<sup>include those</sup> ~~are~~<sup>are</sup> used for making the parts and structural materials for automobile, ~~an~~<sup>an</sup> automobile, ~~tob~~<sup>tob</sup> bicycle, scooter, television, radio, audio equipment, washing machine, rice cooker, personal computer, portable telephone, game machinery, building materials, office supplies, stationery, ~~toys~~<sup>toys</sup>, sports goods, sports equipment, agricultural ~~to~~<sup>to</sup> tools ~~ots~~<sup>ots</sup> and marine tools by the ~~method~~<sup>method</sup> of injection molding, blow molding, ~~compre-~~<sup>compre-</sup> ~~ion~~<sup>ion</sup> molding, slush molding, fluidized bed coating, flat film extrusion ~~proce-~~<sup>processing</sup>

sing and the inflation tubular film  
~~process~~ ~~processing~~

The material of mold may be metal or  
ceramies ceramic

Plastics and gum which are processed by  
using the metallic mold of the present  
invention are thermoplastics and ~~thermo-~~  
~~setplastics~~ as follows.

As the thermoplastic resin, there can  
be used high density polyethylene, high  
pressure low density ~~polyethylene~~ <sup>polyethylene</sup> such ~~vinylalcohol~~  
as HP-LDPE, EVA, EEA, Ionomer, olefin ~~vin~~ <sup>vinylalcohol</sup>  
~~ylalcohol~~ copolymer, LLDPE, VLDPE, ~~poly-~~ <sup>polypropylene (PP)</sup>  
~~propylene (PP)~~, polystyrene (PS), ~~poly-~~ <sup>polypropylene (PP)</sup>  
acrylonitrile-butadiene-styrene ~~copoly~~ <sup>copoly</sup> ~~copolymer (ABS)~~  
~~mer (ABS)~~, acrylonitrile-styrene copolymer  
(AS), acrylonitrile-butadiene copolymer,  
acrylonitrile acrylate-styrene copolymer,  
polyvinyl chloride (PVC), polyamide, ~~poly-~~ <sup>poly-</sup> ~~methylmethacrylate (PMMA)~~  
~~methylmethacrylate (PMMA)~~, polyacetal (POM),  
aminopolyacrylamide, polyarylate, ~~fluoro~~ <sup>fluoro</sup> ~~carbon~~ <sup>carbon</sup>  
~~carbon~~ resin, polyimide (PI), ~~poly-~~ <sup>poly-</sup> ~~amino~~ <sup>amino</sup> ~~bismaleimide (PAI)~~  
~~bismaleimide (PAI)~~, polyamideimide (PAI),  
polyetherimide (PEI), bismaleimidetriazine  
resin (BT), polysulfone, polybutylene  
terephthalate (PBT), polyethylene ~~tereph-~~ <sup>terephthalate (PET)</sup>  
~~thalate (PET)~~, polyvinylidene chloride,  
polycarbonate (PC), polyvinyl acetate,  
polyvinyl alcohol, polyvinyl ether,  
polyvinyl formale, modified PPE, modified  
polyphenyleneoxide (PPO), ~~poly-~~ <sup>poly-</sup> ~~phenyleneoxide (PPO)~~  
~~phenyleneoxide (PPO)~~, polyetheretherketone (PEEK), ~~poly-~~ <sup>poly-</sup> ~~etheretherketone (PEEK)~~  
~~etheretherketone (PEEK)~~, polyarylsulfone (PAS) ~~poly-~~ <sup>poly-</sup> ~~arylsulfone (PAS)~~  
~~arylsulfone (PAS)~~, polyarylsulfone (PA-  
S), polymethylpenten (TPX), liquid crystal ~~polymer~~ <sup>liquid crystal</sup> ~~polymer~~  
~~polymer~~, silicone resin, natural rubber (N  
R), butyl rubber (IIR), ~~acrylonierile~~  
~~acrylonierile~~ <sup>acrylonierilebutadiene</sup>

butadiene rubber (NBR), chloroprene rubber (CR), styrene butadiene rubber (SBR), butadiene rubber (BR).

As the thermoset <sup>thermoplastic</sup> plastic resin, there can be used phenolic resin, urea resin, melamine resin, diallyl phthalate resin, epoxy resin, unsaturated polyester resin, ~~and the~~ like.

The plastic molded products made by using the above mentioned resins are ~~materials~~ used for the parts and structural materials for automobile, automobile, scooter, television, radio, audio equipment, washing machine, rice cooker, personal computer, portable telephone, game machine, machinery, building materials, office supplies, stationery, toys, sports goods, sports equipment, agricultural tools and marine tools.

They are usually prepared by plastic processing methods such as injection molding, blow molding, compression molding, transfer molding, rotating molding, slush molding, inflation tubular film ~~process~~ <sup>processing</sup> and extrusion molding.

The release <sup>agent</sup> of the present <sup>invention</sup> ~~are~~ prepared using one or more than one kind of borate ester of polyoxyalkylene.

The release agent may contain amino group containing <sup>Compounds</sup> and/or solvent <sup>solvents</sup>.

The release agent may further contain surface active agent, pigment, <sup>and</sup> ~~and~~ inorganic organic filler, dripping preventable agent, precipitation preventable agent, antioxidant and deformer.

antioxidants deformers

*agents*  
The release agent may be filled in the aerosol container with propellant.

Coating of the release agent of the present invention *onto surfaces* of the metallic *mold* can be conducted by brush *brushing* *agents*, spraying, dipping or contacting the surfaces with woven cloth or nonwoven cloth which are *has been* immersed with the release agent *agents*.

## EXAMPLE

*agents*  
Now, the release agent for metallic mold for forming a plastic molded product according to the present invention will be described in further detail with reference to Examples.

However, it should be understood that the present invention is by no means restricted by such specific Examples.

### Example 1

Borate ester of polyoxyalkylene expressed by chemical formula (5) was obtained by following synthesis process.

In a 7000 ml flask equipped with three inlet *pipes* and displaced by nitrogen gas were charged 146g (1 mole) of triethyl borate  $[B(OC_2H_5)_3]$ , 1.2g of dibutyl tin dilaurate and 500 ml of benzene.

Subsequently, to the solution in the flask was added with 664g (2 mole) of tripropylene glycol triethylenglycol monomethyl ether and 318g (1 mole) of *propylene glycol* triethylenglycol under stirring condition to obtain a uniform blended solution.

Subsequently, the solution in the flask was stirred for 13 hours at 95°C under the condition of distillation to remove ~~of~~ ethanol and benzene as the ~~by~~ <sup>conditions</sup> by product ~~product~~ <sup>and</sup> to obtain 989g (0.99 mole) of a borate ester of polyoxyalkylene expressed by chemical formula (5).

In a vessel, 100 parts by weight of a borate ester of polyoxyalkylene expressed by chemical formula (5), 15 parts by weight of triethyl amine and 10 parts by weight of ethanol were blended for 10 minutes <sup>at</sup> room temperature to obtain the release agent (1).

The release agent (1) was brushed <sup>onto</sup> the surface of a metallic mold for injection molding of polyacetal (POM) resin composition (made by Polyplastic Company Ltd.).

Using above mentioned metallic mold and resin composition, injection mold molding was conducted.

The terms of maintaining the release agent remained effective on the surface of the metallic mold was about 55 hours, the term "effective time period" which was very long compared to a conventional release agent as shown in the comparative example 1.

The words "The terms of maintaining the release effect of the metallic mold" means the terms from starting time to stopping time of injection molding with the stopping time which is the time of being observed any one item of the following phenomena are observed: such as accumulating of dirty materials on the surface of metallic mold; clouding of the surface of the metallic mold;

~~transferring~~ <sup>contaminants</sup> the shape or contaminant from the metallic mold to the plastic molded product, or transferring contaminants from the metallic mold to the plastic molded product

### Comparative Example 1

According to the same preparation method of Example 1, a release agent (2) consisting 100 parts by weight of high viscosity silicone oil (500 cs at 25°C) and 20 parts by weight of the chlorinated type solvent was prepared.

The same <sup>this release agent was tested</sup> releasing test was conducted according to the same <sup>procedure as</sup> condition of example 1.

The terms of maintaining the release agent on ~~effect of the metallic mold of comparative example 1~~ was about 10 minutes.

### Example 2

Borate ester of polyoxyalkylene expressed by chemical formula (8) was ~~expressed~~ prepared according to the same ~~preparation~~ method ~~(1)~~ except using pentaethylene-glycol ethylether <sup>was used</sup> instead of tripropylene-glycol triethylenglycol monomethyl ether and tripropylene-glycol triethylenglycol. Then a release agent (3)

Then, a release agent (3) consisting 100 parts by weight of borate ester of <sup>polyoxyalkylenes</sup> polyoxyalkylene expressed by chemical formula (8) and 20 parts by weight of the pentaethylene-glycol was prepared.

The same <sup>this release agent was tested</sup> releasing test was conducted according to the same condition of procedure as

example 1.

~~effective time period of this  
The terms of maintaining the release agent  
effect of the metallic mold on the metallic mold of example 2  
was about 48 hours, the terms which was  
very long as compared to the conventional  
release agent as shown in the  
comparative example 1.~~

Example 3

Borate ester of polyoxyalkylene expressed by chemical formula (14) was prepared according to the same preparing method ~~except using pentacosaethylene glycol instead of tripropylene glycol~~ tripropylene glycol triethyleneglycol monomethyl ether and tripropylene glycol triethyleneglycol.

Then, a release agent (4) consisting 100 parts by weight of borate ester of ~~polyoxyalkylene~~ polyoxyethylene expressed by chemical formula (14) and 20 parts by weight of the polyoxyethylene (9) dilauryl amine was prepared.

~~this release agent was tested  
The same releasing test was conducted  
according to the same condition of example 1.~~

~~effective time period of this  
The terms of maintaining the release agent  
effect of the metallic mold of example 3  
was about 65 hours, the terms which was  
very long as compared to the conventional  
release agent as shown in the comparative  
example 1.~~

## ABSTRACT

A release agent for metallic mold for forming a plastic molded product characterized by containing a borate ester of polyoxyalkylene.